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(54) **A method for polishing semiconductor wafers with montmorillonite slurry.**

(57) Semiconductor wafers are polished with an abrasive slurry which is prepared by dispersing montmorillonite clay in deionized water. The pH of the slurry is adjusted to 9.5. to 12.5 by adding alkali such a NaOH or KOH. An oxidizing agent need not be included in the slurry.

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A METHOD FOR POLISHING SEMICONDUCTOR WAFERS WITH MONTMORILLONITE SLURRY

Technical Field

This invention relates to the polishing of the surfaces of semiconductor wafers. In the production of semiconductor devices, polished silicon wafers free of undesirable crystal defects and surface imperfections are a basic requirement. In a typical process for fabricating semiconductor devices,
5 the surfaces of the wafers are polished and cleaned at the last step in the process of preparing the wafers.

Background Art

In the prior art, semiconductor wafers, particularly silicon wafers, have been polished by silica based slurries using many different types of polishing machines. Although a number of improvements have been made to the silica based slurry, there has been no substitute to colloidal silicon dioxide for achieving an acceptable degree of perfection.

A typical abrasive slurry for polishing silicon wafers is taught in U.S. Patent No. 4,057,939; the slurry comprises colloidal SiO_2 admixed with 15 Na_2CO_3 and an oxidizing agent such as sodium dichloroisocyanurate. It is believed that the polishing mechanism is due to the rapid oxidation of silicon to SiO_2 by the polishing slurry component, followed by softening of SiO_2 thus formed to give silica gel (Si(OH)_4) which, in turn, further absorbs the slurry components and becomes softer and is easily removed by 20 the scrubbing action of the polishing slurry. Thus, the polishing mechanism is chemical-mechanical.

Polishing may be effected in machines such as described in U.S. Patent No. 3,691,694 including modifications thereof in accordance with the planetary configuration shown in IBM Technical Disclosure Bulletin,
25 pp. 1760-1761, Vol. 15, No. 6, November 1972.

It is also known that montmorillonite minerals have been mined in a large volume and have been used as a binder for sand in foundry molds and as a thickener for oil-well drilling muds. "The Colloid Chemistry of Silica and Silicates" by R. G. Iler, pp. 190-199, Cornell University Press, 1955
30 describes the chemical structure and nature of montmorillonite minerals.

U.S. Patent 3,966,432 entitled "Liquid Abrasive Compositions Containing A Silicate Suspending Agent" teaches that natural and synthetic clays including hydrophobically treated montmorillonite can be used as a

suspending agent for abrasive material for cleaning hard surfaces of such materials as stainless steel, ceramics and vitreous enamel. The abrasive materials listed are calcite (ground marble), silica, felspar, pumice, 5 kieselguhr and labradorite.

U.S. Patent 4,169,796 teaches that sodium montmorillonite clay when it is mixed with dicalcium phosphate and distilled demineralized water creates an effective and useful shaving lotion and a product for polishing and cleaning dentures.

10 Nonetheless, there has been no attempt in the known prior art to utilize montmorillonite clay in the manufacture of semiconductor devices, particularly for polishing semiconductor wafers.

Disclosure of Invention

It is an object of the present invention to provide a new slurry 15 composition for polishing semiconductor wafers.

It is another object of the invention to provide a substitute for silica based slurries.

It is a further object of the invention to provide a polishing agent for semiconductor wafers which does not degrade polishing pads.

20 It is still another object of the invention to provide a relatively inexpensive polishing slurry for semiconductor wafers.

There are two approaches that are generally used to polish silicon wafers. The first approach involves a two step process. Step one of the two-step process entails the use of highly applied pressure to the workpiece for 25 rapid stock removal. Step two is done at low pressures for a short time and is done primarily for cosmetic purposes, though in some instances, it may also be used to remove superficial surface damage.

The second approach is a single step process performed at low pressure and longer times. This approach can be applied to a single-sided or 30 simultaneous two-sided free polishing.

Low applied pressure generally means that the applied load on the workpiece is less than 69kPa (10psi). High pressure polishing means that an applied load is in excess of that amount and as high as 552 kPa (80psi). The slurry of the present invention can be used in all variations 35 of polishing, with different types of high and low pressure polishing machines and with all types of polishing pads.

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In accordance with the present invention as claimed, the polishing slurry comprises montmorillonite, deionized water and an alkali such as sodium hydroxide or potassium hydroxide. The polishing slurry is prepared by slowly adding two to ten percent by weight of montmorillonite powder

- 5 to deionized water with continuous stirring to form a colloidal suspension. The pH of the suspension is then adjusted to a value in the range of 9.5-12.5 by monitored addition of sodium or potassium hydroxide solution.

In the polishing operation, NaOH or KOH reacts with silicon to form Na_2SiO_3 or K_2SiO_3 which is mechanically removed by montmorillonite.

- 10 With a value of pH higher than 12.5, the silicon surface tends to be excessively etched, which makes it difficult to achieve a smooth and flat surface. When pH is lower than 9.5, effective polishing is hard to achieve because of the low level of chemical reaction.

Since an oxidizing agent such as NaOCl need not be included in the
polishing slurry of the invention, the problem of oxidizing agent induced
pad degradation is eliminated. The present invention provides a second
source for semiconductor polishing slurry, which is much less expensive
than the conventional silica based slurry.

Best Mode for Carrying Out the Invention

- 20 Montmorillonite clay which is available under the trade name of GELWHITE
(Trademark) from Georgia Kaolin Co., is added slowly to deionized water
to form a colloidal suspension. The pH of the suspension is adjusted to
the value of 11.5 for low pressure polishing and to 12.0 for high pressure
polishing. Silicon wafers having a diameter of 82.5 mm are polished with
25 the slurry utilizing a free polisher which is substantially described in
the aforementioned U.S. Patent 3,691,694.

The free polisher comprises a rotatable platen having a polishing cloth on the upper surface upon which a mask having suitable apertures therein for receiving wafers is positioned. A hoop is connected to the mask for

- 30 imparting rotation thereof separately from the rotation of the platen. Overlying the mask and wafers is an upper plate having a polishing cloth thereon for applying a uniform pressure upon the opposite surface of the wafer. The upper plate is separately driven so that upon rotation of the platen, with the hoop and the mask, and the upper plate the opposite
35 planar surfaces of the wafer are brought into coplanarity while being polished.

In the polishing operation, a polishing slurry is provided on the

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polishing cloth at the central portion of the platen by a feed system. As the upper plate turns within the hoop, radially extending grooves in the plate catch excess slurry and due to the centrifugal force caused by rotation of the plate they tend move the slurry outwardly. In this manner 5 excess polishing slurry is removed from the platen and caught in a suitable container for reprocessing and reuse if desired. During polishing, wheel speeds may vary from 40 rpm to 60 rpm, optimum at 55 rpm.

Tables I and II show the conditions used in low pressure polishing and high pressure polishing respectively.

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TABLE I

<u>Pressure (kPa) (psi)</u>	<u>pH</u>	<u>Slurry Flow Rate (cc/min.)</u>	<u>Temp. (°C)</u>	<u>Removal Rate (μm/min.)</u>
17.9	2.6	11.5	500	54
31.1	4.5	11.5	500	42
15 36.6	5.3	11.5	500	42

TABLE II

<u>Pressure (kPa) (psi)</u>	<u>pH</u>	<u>Slurry Flow Rate (cc/min.)</u>	<u>Temp. (°C)</u>	<u>Removal Rate (μm/min.)</u>
255	37	12.0	300	40-90
20 552	80	12.0	300	40-90

The stock removal rates accomplished with this slurry are comparable to the removal rates achieved with the silica based slurry which includes an oxidizing agent such as NaOCl, as disclosed in the aforementioned U.S. Patent 4,057,939. Such oxidizing agent is known to degrade the polishing cloth. 25 Typically the life of the polishing cloth is reduced to one-half when it is subjected to an oxidizing agent.

The slurry flow rate can be any rate in the range of 300 to 500 cc/min. When it is lower than 300 cc/min., the friction between the polishing cloth and the wafers becomes excessive and renders it difficult to run the polisher. 30 A flow rate larger than 500 cc/min, is simply not necessary and it is wasteful.

In the high pressure polishing, the polishing temperature is determined by the friction between the polishing cloth and the wafers, and it can vary from 40 to 90 °C.

35 The mechanism of stock removal is more mechanical in the high pressure polishing so that the applied pressure is the predominant factor for

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controlling stock removal rates. It should be noted that with low pressure polishing, stock removal rates typically are most sensitive to pressure and temperature variations.

After polishing and removal from the polishing ambient, the wafer surfaces
5 are readily cleanable. One singular effect is that the addition of NaOCl
(sodium hypochlorite) at an appropriate time near the end of the polishing
cycle results in a hydrophilic surface after polishing. This ability to
render surfaces hydrophilic, characteristic of hypohalites, facilitates
post polish wafer cleaning. Although an 82.5 mm wafer was used to
10 demonstrate the invention, any size wafer can be polished with the polishing
slurry of the invention.

CLAIMS

1. A method for polishing a semiconductor wafer comprising:
preparing a polishing slurry by dispersing an abrasive powder in
water, and
polishing the wafer with said slurry,
5 characterized by:
selecting montmorillonite clay as the abrasive powder.
2. The method of claim 1 wherein alkali is included in the slurry such
that the pH of the slurry is in the range of 9.5 to 12.5.
3. The method of claim 2 comprising:
10 adding montmorillonite powder to deionized water with continuous
stirring to form a colloidal suspension, and
adding alkali solution to said suspension to adjust the pH in the range
of 9.5 to 12.5.
4. The method of claim 3 wherein 2 to 10 percent by weight of mont-
15 morillonite powder is added to said deionized water.
5. The method of claim 2, 3 or 4 wherein said alkali is sodium or
potassium hydroxide.
6. The method of any previous claim wherein polishing is done under a
low pressure of less than 69 kPa (10 psi) applied to said wafer.
- 20 7. The method of any of claims 1-5 wherein polishing is done under a high
pressure of 207 to 552 kPa (30 to 80 psi) applied to said wafer.
8. The method of any previous claim wherein sodium hypochlorite is added
to the slurry at a time near the end of the polishing cycle.
9. A composition for polishing semiconductor substrates comprising 2 to
25 10 percent by weight of montmorillonite clay added to deionized water,
and alkali sufficient to render a pH value in the range of 9.5 to 12.5.
10. The composition of claim 9 wherein said alkali is sodium or potassium
hydroxide.

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EUROPEAN SEARCH REPORT

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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ?)
A	FR-A-2 414 387 (GRACE) * Claims 3, 4, 8, 9 *	1, 2	H 01 L 21/302
A	CH-A- 505 466 (WACKER) * Claim; subclaims 1, 4; column 1, line 28 - column 2, line 2 *	1, 3, 5, 10	
A	DE-C-1 227 307 (SIEMENS) * Claim 1 *	1, 5	
D, A	US-A-3 966 432 (COLGATE-PALMOLIVE) * Claim 1; abstract *	1	
D, A	US-A-4 057 939 (IBM) * Claim 9; abstract *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. ?)
	-----		H 01 L 21/302 B 24 B 1/00 B 24 B 7/34 G 09 G 1/02
The present search report has been drawn up for all claims			
Place of search BERLIN	Date of completion of the search 04-11-1983	Examiner ROTHER A H J	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone	Y : particularly relevant if combined with another document of the same category		
A : technological background	O : non-written disclosure		
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